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CATALYZED SODIUM CHLORATE CANDLES

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INTRODUCTION

State-of-the-art chlorate candles have been used for decades as emergency oxygen sources in submarines (ref. 1). Reliability in present units is achieved mainly by overdesign (ref. 2), which imposes undesirable weight and volume penalties on portable systems. Recent work at Ames Research Center on basic advances in oxygen storage and regeneration has emphasized catalytic decomposition of sodium chlorate to achieve increased gas purity, lower operating temperatures, and improved reliability.

A typical chlorate candle unit (ref. 1) is illustrated in figure 25.1. A firing device in the ignition assembly starts the ignition cone burning. This in turn initiates the decomposition of the sodium chlorate in the solid composite of the body so that oxygen is released as a hot gas. A clinker of sodium chloride (with the binders used in the composite) remains. The simplified chemistry is represented by (ref. 3):

$$NaClO_3 \rightarrow NaCl + 1.5O_2 \quad (1)$$

$$4NaClO_3 \rightarrow 3NaClO_4 + NaCl \quad (2)$$

$$NaClO_4 \rightarrow NaCl + 2O_2 \quad (3)$$

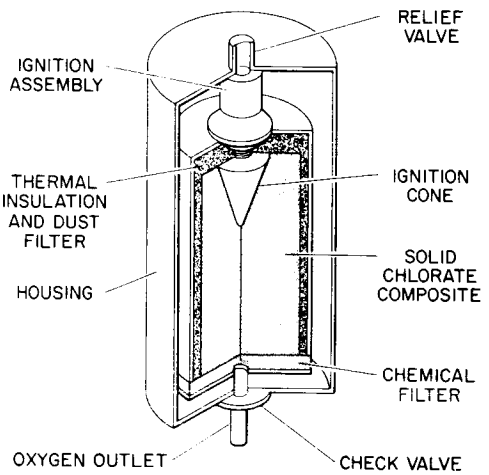


Figure 25.1 *Chlorate candle assembly.*

The sodium chlorate can decompose directly at high temperatures to give sodium chloride and oxygen gas, or to sodium perchlorate, which at a still higher temperature produces the same end products. Side reactions can lead to traces of chlorine that are usually minimized by a suppressor such as barium peroxide. Conventional candles are mixed with a fuel (typically iron powder) and some type of binder. Asbestos fiber, glass fiber, and steel wool have been used as binders. Usually some chemical filtering is used to assure adequate purity of the gas. For example, hopcalite catalyst can be inserted in the effluent line to oxidize traces of carbon monoxide.

EXPERIMENTAL ARRANGEMENTS

Cylindrical segments, 1 in. diam by 1 in. length, were used for most of the survey work on optimizing composition using a catalyst. These short candles are the subject here. Sodium chlorate was purified by recrystallization, followed by drying and grinding. Chemical analysis showed 0.017-percent carbon, with water <0.05 percent and chlorite <0.003 percent. All candle segments were mixed using 6 wt percent silicon dioxide fibers as a binder, which is a standard procedure reported to have a mildly catalytic effect on chlorate decomposition (ref. 4). Cobalt metal powder

was used as a fuel. The supplier's (African Metals Corporation) analysis listed impurities as 0.035-percent carbon, 0.020-percent calcium, 0.010-percent sulfur, 0.005-percent silicon, 0.025-percent iron, 0.026-percent nickel, and traces of calcium, magnesium, and manganese. Catalysts often were used in addition to or in place of the fuel. The ingredients were mixed by hand in a dry inert gas atmosphere and pressed to 40,000 lb in a single ram press. The findings of Gustafson et al. (ref. 5) that only trapped water leads to chlorine evolution and that glass fiber increases production of chlorine have not been tested. Chemical filters and chlorine suppressors were not used in this work because one object was to learn whether purity and dryness would be adequate to keep free chlorine within acceptable limits.

Uniform mixing of candle ingredients varying in particle size and density is difficult. Early candles contained small white lumps presumed to be almost pure sodium chlorate. Chemical analyses of fractional gram portions excluding these visible anomalies showed that the catalyst also was distributed nonuniformly. Better blending of materials greatly improved homogeneity (table 25.1). The later candles (represented by the 6.7 percent fuel, no catalyst formulation in this table) did not have the white lumps and showed much more uniformity. This better mixing markedly improved the reproducibility of candle segment performance and the smoothness of burning.

Table 25.1 *Test of candle uniformity.*

EARLY CANDLE % CATALYST	LATER CANDLE % COBALT
5.76	6.78
5.91	6.75
3.75	6.59
3.75	6.67
3.71	6.46
3.76	6.76
3.88	6.63
4.50±0.91	6.66±0.09

CHEMICAL ANALYSIS OF APPROXIMATELY 0.2 gm PORTIONS OF CANDLES, SELECTED AT RANDOM (EXCLUDING LUMPS OF PURE SODIUM CHLORATE)

Many catalysts have been proposed (refs. 5-8) for thermal decomposition of chlorates. The effects of cobalt chloride and cobalt oxide are shown in figure 25.2. The percentage of available oxygen W in the material is plotted against the temperature to show the extent of the decomposition. Sodium chlorate decomposes rapidly near 500° C and sodium perchlorate at a higher temperature. The catalysts lower the decomposition temperatures appreciably. Cobalt oxide was used for most of the studies because cobalt chloride is difficult to dry. Only the results of the cobalt oxide catalysts are reported. In addition to the thermogravimetric analyses, differential thermogravimetric studies and differential scanning calorimetry of candle chips weighing a few milligrams were performed.

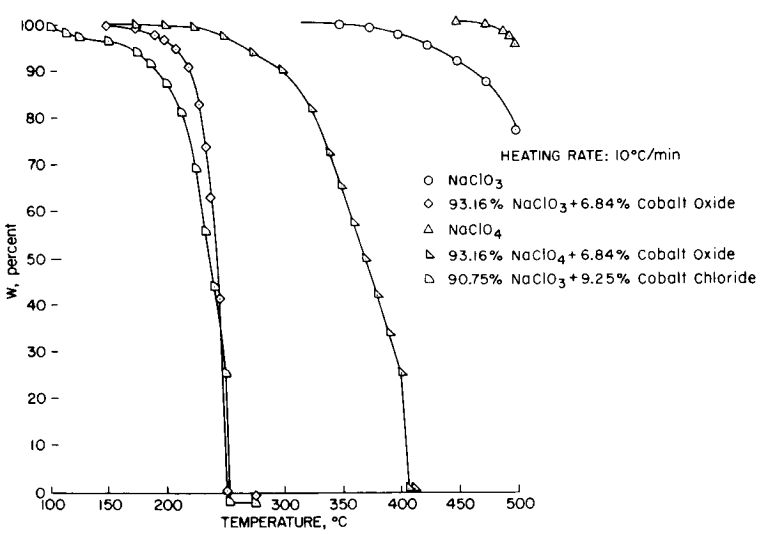


Figure 25.2 *Catalytic decomposition of sodium chlorate and perchlorate.*

The 1-in. candle segments were generally capped by a 35 percent cobalt-fuel-rich ignition section. Ignition was accomplished by electrical heating of a platinum wire incorporated in the ignition

section. Burning was usually done with no thermal insulation, with the segment completely insulated by firebrick or with a standardized partial insulation. Internal temperatures were measured by chromel-alumel thermocouples inserted 0.25 in. into the candle. Linear burn rates have been calculated from the burn time for complete segments or portions of segments. The decomposition rate depends critically on heat transfer characteristics. More elaborate studies are planned to design containers for practical candle units.

DIFFERENTIAL SCANNING CALORIMETRY

One of the major analytical tools of this study has been differential scanning calorimetry (DSC). The net rate of heat release from the exothermic decomposition of chlorate as a function of temperature is a measure of the rate of production of oxygen. Figure 25.3 shows DSC results for a chip from a candle made with 5 percent cobalt fuel. The baseline is indicated by a dashed line. The endothermic melting of the sodium chlorate occurs near 260° C, followed by exothermic decomposition with peaks around 340° C and 440° C. The studies indicate that the second peak is connected with the decomposition of sodium perchlorate as an intermediate, but this has not yet been shown quantitatively. In addition to the DSC, there is a simultaneous differential thermogravimetric trace (DTG) of the rate of change of weight versus temperature of a similar sample. As expected, there is no weight change during the melting, but the two curves match well during decomposition where the weight loss measures the oxygen evolution.

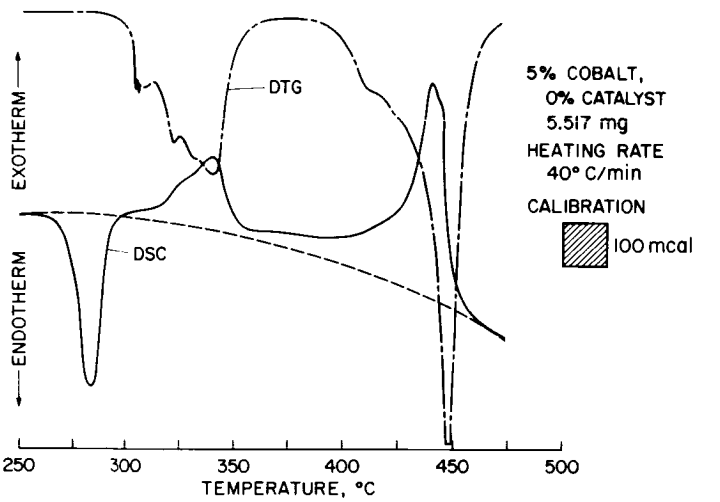


Figure 25.3 *Differential scanning calorimetry of chlorate candle with no catalyst.*

The effect of catalysts on the cobalt-fueled candles is illustrated in figures 25.4 and 25.5. A trace of catalyst lowers the reaction temperature so that the two DSC peaks now appear near 320° C and 370° C. Three percent catalyst shows a single decomposition region around 300° C. Decomposition is essentially complete by 310° C or 315° C.

Some results obtained with candles containing no fuel are presented in figures 25.6 and 25.7. The shape of the curve for 3-percent catalyst with no fuel is similar to that shown in figure 25.5 for a candle containing 3 percent catalyst and 5-percent fuel. The decomposition without fuel is complete below 300° C

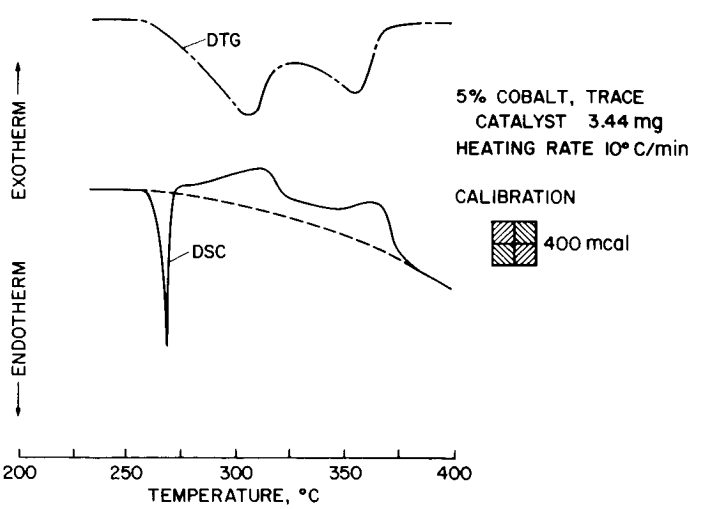


Figure 25.4 *Differential scanning calorimetry of chlorate candle with a trace of catalyst.*

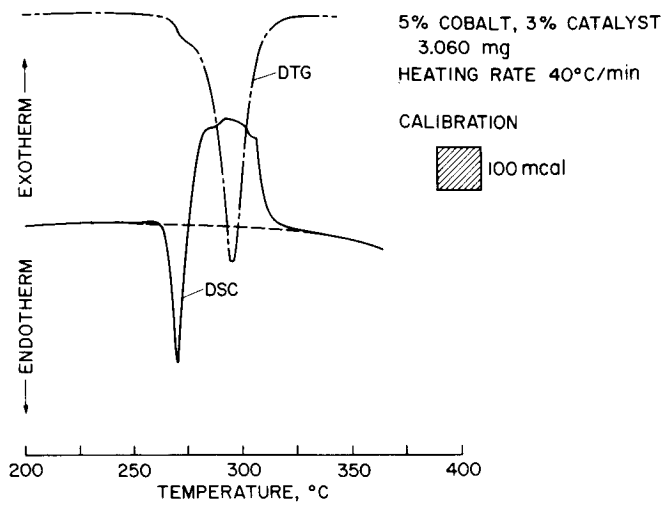


Figure 25.5 *Differential scanning calorimetry of chlorate candle with 3 percent catalyst.*

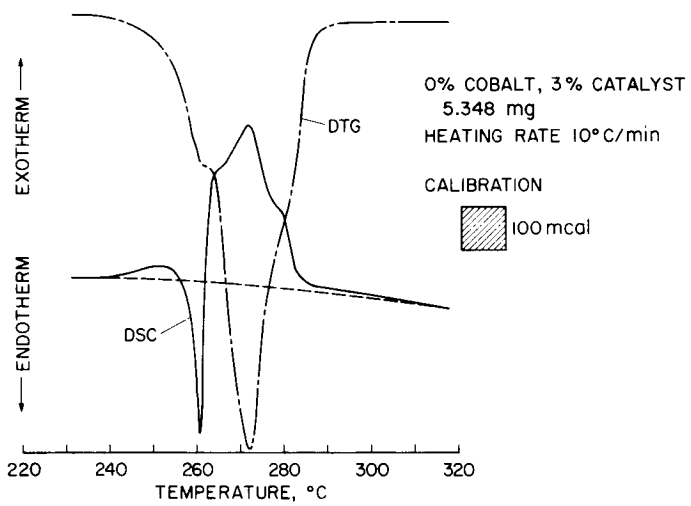


Figure 25.6 *Differential scanning calorimetry of chlorate candle (without fuel) containing 3 percent catalyst.*

at this slower heating rate of 10° C/min. Not all candle segments burn to completion, however, when only 3 percent catalyst is used. Complete burn is achieved with 9-percent catalyst. The DSC in figure 25.7 shows that nearly half the decomposition occurs below the melting point and that the melting endotherm is masked by the exothermic decomposition.

The DSC results depend on the heating rate, sometimes quite strongly, as illustrated in figures 25.8, 25.9, and 25.10, for a 5 percent cobalt, 6 percent catalyst candle. The change in weight versus temperature of similar samples, rather than rate of change or DTG, is shown in addition to the DSC trace. The mass dial numbers are related to the upper limit of the recorded mass in micrograms, and

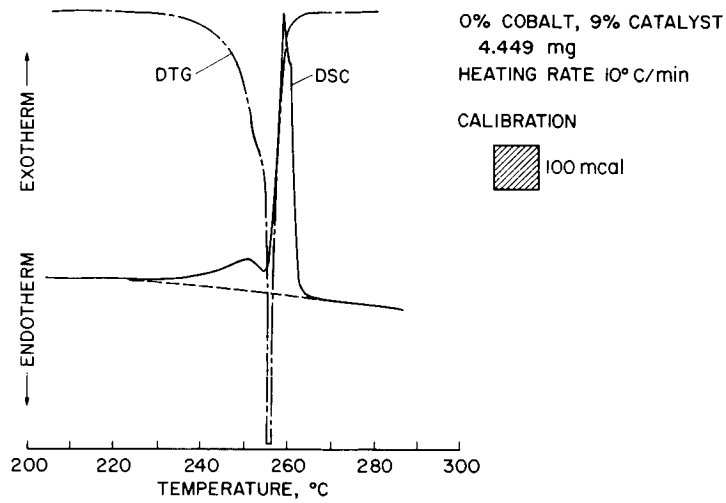


Figure 25.7 *Differential scanning calorimetry of chlorate candle (without fuel) containing 9 percent catalyst.*

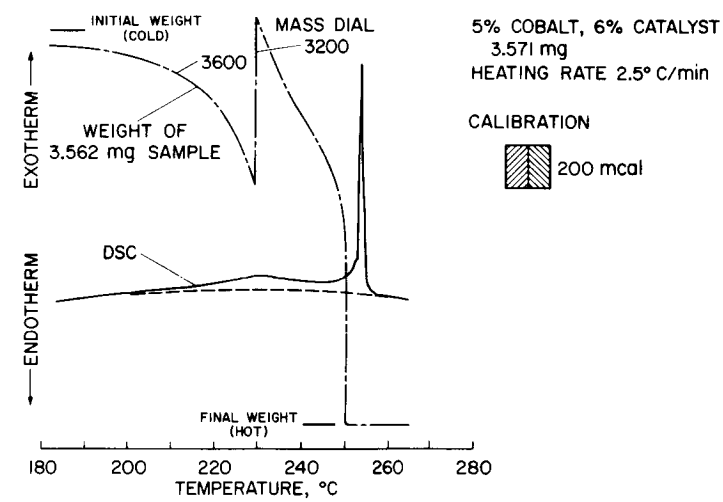


Figure 25.8 *Differential scanning calorimetry of chlorate candle using slow heating rate.*

were shifted by the operator to keep the trace on scale. At a slow heating rate of 2.5° C/min there is extensive decomposition in the solid phase, and less at a rate of 10° C/min. A reduced melting endotherm appears again at the faster rate of 40° C/min. The general appearance of this latter curve is quite similar to the 5 percent cobalt, 3 percent catalyst candle shown in figure 25.5. Even 40° C/min is lower than the heating rate in a burning candle, as discussed in the next section, so further tests at higher heating rates are planned.

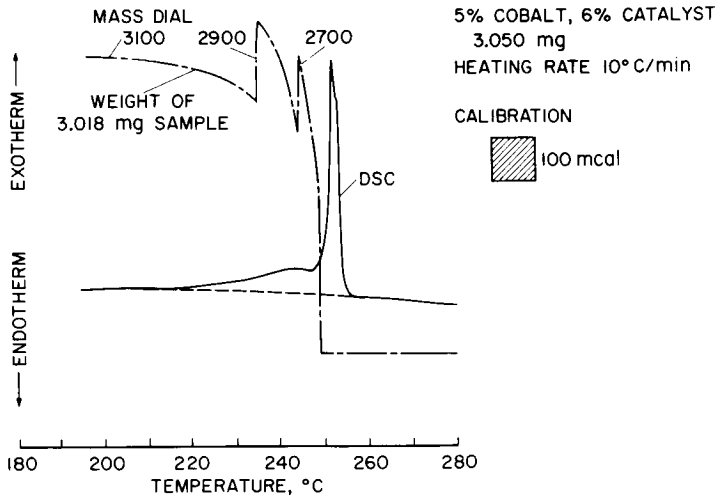


Figure 25.9 *Differential scanning calorimetry of chlorate candle using moderate heating rate.*

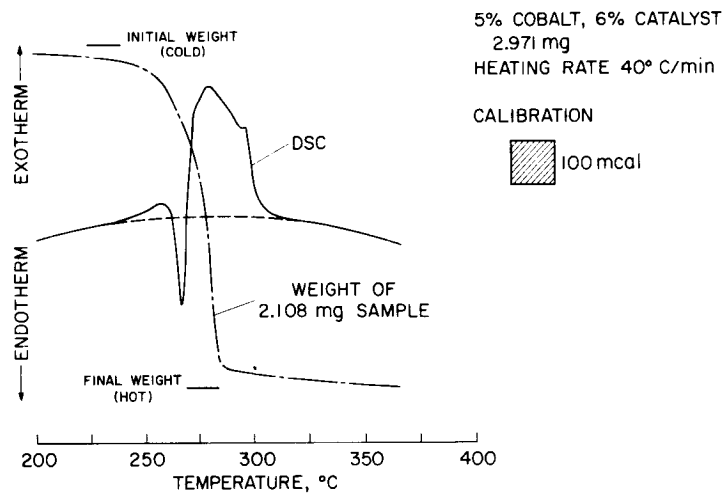


Figure 25.10 *Differential scanning calorimetry of chlorate candle using faster heating rate.*

INTERNAL TEMPERATURES DURING DECOMPOSITION OF CANDLE SEGMENTS

Temperatures recorded by thermocouples inserted 0.25 in. into the burning 1-in. segments are shown in figure 25.11 for uncatalyzed compositions and in figure 25.12 for the 5 percent cobalt, 3 percent catalyst short candles. Two temperatures from two thermocouples at different locations are measured simultaneously with a dual pen recorder. Heating of roughly 100° C/min arises from conduction in advance of the burn front. This rate is much accelerated just as the decomposition zone reaches the thermocouple. The temperature does not increase rapidly above the melting point of sodium chlorate for a while, especially in the uncatalyzed segment. The endothermic melting absorbs much of the heat released during early decomposition and stabilizes the temperature. The maximum temperature is recorded considerably later than the beginning of decomposition at the

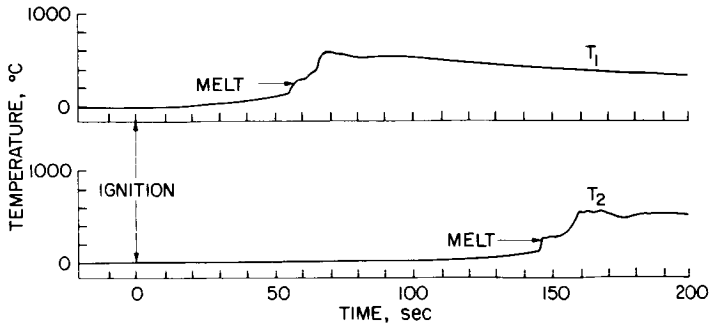


Figure 25.11 *Internal temperatures during decomposition of chlorate candle without catalyst.*

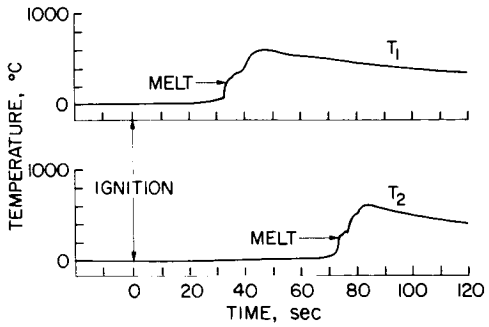


Figure 25.12 *Internal temperatures during decomposition of chlorate candle with 3 percent catalyst.*

thermocouple (the DSC results show appreciable reaction near the melting point). Frequently expansion of the clinker causes erratic cooling after this maximum. It is important to realize that the maximum temperature is reached after decomposition is complete, by conduction of heat from adjacent portions of the candle. Heat losses cause considerable variation in the maximum temperatures recorded. These losses are greater in slowly burning segments than in rapidly burning segments. Very large voids are occasionally seen in clinkers of incompletely burned candles, which seems to indicate that temporary excessive cooling may have extinguished the segment. Maximum temperatures in catalyzed candles are reached rather quickly after melting, and burning is generally smoother than with uncatalyzed candles. Some average maximum temperatures of candle segments insulated in firebrick are tabulated in table 25.2. The lowest temperature of 560° C (for candle formulations burning completely) was obtained with no fuel in a 9 percent catalyst segment. The other formulations listed here contained no catalyst. The rather limited variation in average maximum temperature from 630° C to 700° C as the fuel content is increased from 3 to 7 percent is due partly to heat losses and probably also to incomplete combustion of the fuel (ref. 1). The highest fuel concentration studied, 35 percent cobalt, gave an average maximum temperature of 1110° C while oxidizing the fuel nearly completely to cobalt oxide based on measurements of weight change and oxygen yield. The carbon monoxide production was greater for segments burning at higher temperatures, probably because of the greater stability of carbon monoxide relative to carbon dioxide at higher temperatures. Further observations on gaseous contaminants and candle temperatures are given in a subsequent section.

Table 25.2 *Maximum internal temperatures during burning of chlorate candles without catalyst, insulated with firebrick.*

COBALT, %	T_{max}, °C
0	560
3	630
5	670
7	700
35	1110

Additional internal temperature measurements are presented in table 25.3, which shows the effect of insulation on burn rate and maximum temperature for both catalyzed and uncatalyzed compositions. Results are enclosed in parentheses when only a portion of the samples burned completely. Burn rates for these less complete tests, although consistent, are considered less reliable. Also, maximum temperatures are abnormally low when a candle goes out near the thermocouple, even if burning has progressed beyond this point. No obviously abnormal data have been included,

but the results should be used with caution. The variation in average maximum temperature with insulation is quite limited, indicating that 0.25-in. inside the clinker generally shielded the thermocouple adequately from outside influences. The burn rate depends markedly on insulation, while internal temperatures do not. The uninsulated burning in this study was not as successful as that reported in reference 7, perhaps because this work was done in a hood where the airflow may have produced appreciable cooling or because of some unexplained variation in components.

Table 25.3 *Effect of insulation on chlorate candle burning.*

COBALT, %	CATALYST, %	INSULATION	BURN RATE, mm/sec	MAXIMUM INTERNAL TEMPERATURE, °C
5	0	NONE	(0.08)	(640)
5	0	PARTIAL	(0.11)	(640)
5	0	COMPLETE	0.21	670
5	3	NONE	(0.17)	(540)
5	3	PARTIAL	0.20	600
5	3	COMPLETE	0.34	640

The trend of maximum temperature with fuel concentration is tabulated in table 25.4 for candles containing 3 percent catalyst. Temperatures are slightly lower than the uncatalyzed candles of table 25.2. As before, the low temperatures below 500° C are probably not reliable because of incomplete burning. The internal temperatures with higher fuel concentrations indicate heat losses and possibly incomplete combustion, as before. Burning proceeds steadily with less fuel when catalyst is used. Since the heat of combustion of the fuel in typical commercial candles is about equal to that generated by the chlorate decomposition, savings of up to a factor of 2 are anticipated with catalyzed candles containing minimal fuel. Quantitative calorimetric measurements are needed in addition to the internal temperatures to accurately determine the savings. Calorimetric data also contribute significantly in the design of an insulated container.

Table 25.4 *Effect of fuel concentration on chlorate candle burning.*

COBALT, %	CATALYST, %	BURN RATE, mm/sec	MAXIMUM INTERNAL TEMPERATURE, °C
0	3	(0.19)	(480)
1	3	(0.25)	(490)
3	3	0.36	560
5	3	0.34	640

PURITY OF GENERATED GAS

There is a definite correlation between burn temperature and the amount of impurities produced. All segments had a slight aerosol of sodium chloride particles in the effluent oxygen (based on visual observations). Few quantitative measurements have been made of these solids, but their volume clearly is far less than that of the smoky gas from the few iron-fueled commercial candles tested, which burned at higher temperatures. All experimental compositions produced detectable amounts of chlorine, and the chlorine odor increased with temperature. Additional heating of candle clinkers with a torch increased the amount of chlorine, also indicating the effect of high temperature on contaminant production. The chlorine contamination will not be reported until an absolute calibration is performed for the mass spectrometer used for the most precise purity measurements. The reactivity of chlorine is apparently so great that low measured values are suspected.

Results of mass spectrographic analyses of three formulations—a high temperature starter with 35 percent cobalt and no catalyst; a 5 percent cobalt, 3 percent catalyst composition with a starter section; and a no-fuel, 9 percent catalyst segment made without a starter—are given in table 25.5. The 1110° C starter produces 95 ppm of carbon monoxide and the no-fuel, no-starter segment only

1 ppm of carbon monoxide. The other segment showed 13 ppm of carbon monoxide, most of which probably came from the starter material. The carbon dioxide measurements indicate probable complete combustion of the carbon impurities in the candles. Total carbon calculated from chemical assays of the ingredients ranges from 0.018 to 0.025 percent. The greater variation of 100 to 2500 ppm carbon dioxide in the mass spectrographic analyses is largely due to the low yield of total gas from the fuel rich starter; most of the oxygen produced is consumed in combustion of the fuel, increasing the concentration of a given quantity of impurities. Thus it is important to keep total carbon content low to limit carbon dioxide contamination, and to have a candle formulation burning at a low temperature to minimize the more toxic carbon monoxide contamination. Minimizing fuel also increases the total yield of oxygen and decreases the concentration of contaminants.

Table 25.5 *Mass spectrographic measurements of gaseous contaminants in oxygen generated by chlorate candles.*

COMPOUND	STARTER (35% Co) ppm	(A) 5% Co 3% CATALYST ppm	(B) 0% Co 9% CATALYST ppm
CARBON MONOXIDE	95	13	1
CARBON DIOXIDE	2500	100	170
METHANE	< 7	<7	< 1
ETHANE	< 0.5	0.4	0.02
ACETYLENE	< 0.05	<0.02	<0.01
ETHYLENE	< 0.02	<0.02	<0.01
C_3 AND HIGHER HYDROCARBONS	17	<0.2	<0.1
NITROUS OXIDES	< 0.05	<0.05	<0.1
HALOGENATED COMPOUNDS	< 0.05	<0.1	<0.1
SULFUR DIOXIDE	< 0.02	<0.01	<0.01
HYDROGEN CHLORIDE	< 0.02	<0.09	<0.01
CARBONYL SULFIDE	< 0.01	<0.01	<0.01
CARBON DISULFIDE	< 0.01	<0.01	<0.01
HYDROGEN	<20	<20	<20
METHYL CHLORIDE	—	—	0.04
CHLORINE	PRESENT*	PRESENT*	PRESENT*

*MEASUREMENTS OF REACTIVE GASES CONSIDERED UNRELIABLE
(A) 6 gm STARTER AND 30 gm BODY
(B) 36 gm BODY - NO STARTER

The only other considerable contaminant is 17 ppm of higher hydrocarbons from the high temperature starter. This observation underscores the efficacy of high purity ingredients and low decomposition temperatures in keeping dangerous gases to tolerable limits. Dryness of the chemicals has not completely eliminated the annoyance of chlorine odor, and use of a suppressor is probably better than further efforts at purifying candle segment ingredients.

Much confusion has arisen in the past over acceptable levels of contaminants in breathing oxygen. Toxicity is an important criterion in setting limits, but other factors such as explosive mixtures and objectionable odors also need consideration. Physiological tolerances in short duration emergency oxygen supplies can be less stringent than those applied to continuous long-term supplies, while physical safety factors may be greater if the emergency supplies are to be used in extreme environments such as firefighting. Purity specifications derived for one intended use often cannot satisfactorily be applied to other situations without modification.

The specifications listed in table 25.6 illustrate some of the foregoing points. The portable environmental control system (PECS) requirements taken from reference 7 are quite stringent and seem to be based on out-gassing limitations for closed systems. The carbon dioxide and carbon monoxide values of 5 ppm for PECS are easily obtainable in compressed gas from liquid air plants, so it is perhaps reasonable (and economically feasible) to specify this purity for tank oxygen. The carbon dioxide limit can be increased by a factor of 100 without physiological harm, so it is not reasonable to apply the same standards to chemical oxygen sources for use in open-loop systems, for example, without some consideration of the economics and the complexity of design. Other partial specifications are also listed in table 25.6 for guidance in potential applications of chlorate candle oxygen generators. Reference 11 gives a more extensive list with some discussion of the relative importance of various potential contaminants. It does not seem appropriate to select arbitrary purity standards at this stage of development of this candle. Some filtering is necessary with present formulations, and gas scrubbing or the equivalent is needed in closed-loop systems to maintain carbon dioxide and water vapor within physiologically acceptable limits. A good design

will balance the various factors to optimize the intended use, rather than work to arbitrary limits.

CONCLUSIONS

Appropriate catalysts can lower the effective decomposition temperature of sodium chlorate to near its melting point, permitting major improvements in the design of conventional chlorate candles. This has been verified by the complete burning of units made without fuel, using two different batches of cobalt oxide catalyst. Even more dramatic has been the initiation of the decomposition with a hot wire igniter without using high fuel starter material. Each of a set of five candles was successfully ignited with about 10 W of low voltage power. Combustion was too slow in the laboratory model for practical use as an emergency supply. However, it is a straightforward matter to substitute catalyst for most if not all the fuel in a conventional starter cone and greatly reduce the contaminant levels while obtaining a fast start.

Table 25.6 *Some breathing oxygen specifications giving limits for certain contaminants.*

CONSTITUENTS	ALLOWABLE LEVEL IN ppm BY VOLUME		
	PECS (A)	SAE (B)	NAS/NRC (C)
ACETYLENE, C_2H_2	0.02		6000
CARBON DIOXIDE, CO_2	5.0	1000	5000
CARBON MONOXIDE, CO	5.0	25	15
HYDROCARBONS (C_3H_3 AND HIGHER)	1.0[§]		*
ETHANE, C_2H_6	2.0		*
ETHYLENE, C_2H_4	0.2		*
HALOGENATED COMPOUNDS	0.1		VARIED
METHANE, CH_4	25.0		13,000
NITROUS OXIDE, N_2O	1.0		

[§]HEXANE EQUIVALENT
*ALIPHATIC HYDROCARBONS 60 mg/m^3, AROMATIC HYDROCARBONS 10 mg/m^3 (BENZENE 3 mg/m^3)
(A) REFS 7 AND 9 (B) REFS 9 AND 10 (C) REF. 11, 90-DAY EXPOSURE LIMIT FOR SPACE CABINS OR SUBMARINES

The catalytic effect of cobalt powder on chlorate decomposition has been confirmed. Catalysis is enhanced by oxidation of the metal during burning. Catalysts other than cobalt compounds should also be effective; the complete elimination of fuel has shown that the oxidation of cobalt during decomposition is not a vital factor in the improved performance of catalyzed candles.

Additional work is being done on control of the oxygen production rate. This is a complex function depending on the heat consumed in melting the chlorate, the rate of heat loss to the container and from it to the surroundings, the contact between the catalyst and chlorate, candle composition, and other factors. The design of the container has a considerable influence on the burn rate and is an important factor in the design and production of a practical candle unit.

Gas purity has been improved considerably with the catalyzed compositions having lower decomposition temperatures. No further efforts are planned at present to improve oxygen purity, as burn rate could be affected adversely if only gas purity were stressed.

Other applications of the catalyzed chlorate composition are apparent. The increased reaction rate should be quite useful in units with cold start requirements. The amount of catalyst can be varied if nonuniform burn profiles are desired. Effective modulation of the burn rate is much closer to realization, and unconventional designs using a catalyst in chlorate oxygen generators now appear practical.

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